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13. ABSTRACT (Maximum 200 words)  Created new microlayered and nanolayered polymer composites for various novel and unique applications, (1) Produced clear microlayered composites with improved ballistic performance (see attached, interim report 6/1/98-12/31/98). (2) Developed microlayered composites with highly anisotropic conductivity (see attached, interim report 6/1/98 - 12/31/98). (3) Polymer nanolayered systems of polypropylene were created having discoidal, meso-form morphologies. Also, high density polyethylene has been changed to a "shesh-kabab" structure due to the fact that the nano-layer thickness is less than the radius of gyration of the polymer macromolecule (see attached, interim report (1/1/99-12/31/99). (4) High barrier, injection moldable systems have been produced by microlayering a polymer with good water barrier and a polymer with good oxygen barrier. Taking advantage of differences in melting points, layer integrity was maintained during injection molding in between the two melting points. This concept, which utilizes and maintains the large interfacial surface area achieved with microalayering, is broadly applicable to highly immiscible polymeric systems. (see attached, interim report 1/1/00-12/31/00). (5) One-dimensional photonic materials with applications to optical limiting and optical switching have been developed in conjunction with the Naval Research Laboratory. This was accomplished by synergistically combining nanolayer coextrusion methodology with dispersion of nonlinear dyes and careful control of nanolayer refractive indices. (see attached, interim report 1/1/00-12/31/00 and progress to date, 1/1/01-5/31/01).				
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## Progress to date joint with J. Shirk, ONR

1/1/01 – 5/31/01

We have made considerable progress in fabricating and characterizing nonlinear nanolayered optical materials since the initiation of funding. The initial stages, a proof of principle demonstration of the nanolayered materials, is summarized here.

A series of nano-layered nonlinear materials were fabricated both with and without nonlinear dyes in alternate layers. Nanolayered films were fabricated using styrene-acrylonitrile copolymers (SAN), polycarbonate (PC), and polymethylmethacrylate (PMMA) as hosts. A nonlinear dye developed at NRL, PbPc(CP)<sup>4</sup>, and nigrosine were used as the nonlinear dyes. In the initial experiments, SAN was used as a host because a wide range of copolymers is available, each with a slightly different refractive index. This made it easier to control the index modulation in the multilayer polymers.

The presence of nanometer scale layers in the materials we prepared were demonstrated by AFM measurements and by optical characterization. A nanolayered sample with a small index difference between the layers had transmission and reflection properties consistent with a multilayer dielectric reflector.

Figure 1 shows the spectrum of the reflected light from a 4096 layer sample with an average layer thickness of 87 nm compared to that of a sample with a 31 nm average layer thickness. The 87 nm layered film has a first order band gap in the visible and should show a

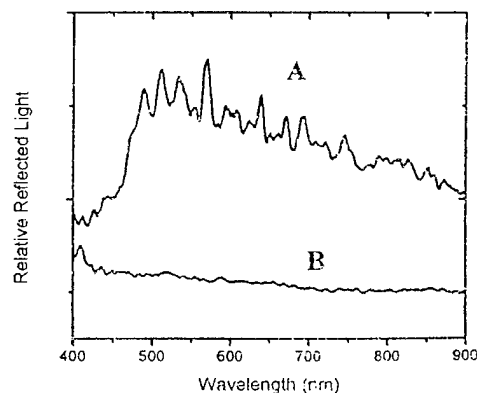


Figure 1. The spectrum of the light reflected from nanolayered styrene-acrylo-nitrile materials with an average layer thickness of (A) 87 nm and (B) 31

reflectivity in this region. The band gap for the 31 nm film is at 197 nm, so the latter sample shows only the unusual Fresnel reflection near 500 nm. The thickness of the individual layers was measured by atomic force microscopy (AFM) and a distribution of thickness was found. The layer thickness distribution derived from the AFM measurements is consistent with the width of the observed reflection spectrum in Figure 1.

Nonlinear transmission and reflectivity was demonstrated in several nanolayered polymeric materials fabricated by dissolving either lead tetrakis(cumylphenoxy)-phthalocyanine ( $\text{PbPc}(\text{CP})_4$ ) or nigrosine into alternate layers of either a SAN or a polycarbonate structure.  $\text{PbPc}(\text{CP})_4$  is known to have a very strong nonlinear absorption and refraction coefficient. The nigrosine has a broad absorption in the visible and an excited state was reported to relax rapidly with the conversion of the absorbed energy into heat. The resulting rise in temperature causes a change in the refractive index. The transmission as a function of incident fluence for a multilayer sample of a polycarbonate with nigrosine showed a drop and then a rise. In these samples, the refractive index,  $n_o$ , of the dyed layers is initially larger than that of the undyed layer. The change in index with fluence of the nigrosine layers is negative so that the transmission decreases until the index is matched, and then it rises as the index difference increases.

The response time of the reflectivity was measured by studying the reflectivity as a function of time after a 1.2 picosecond pump pulse was incident on the sample. One multilayer sample consisted of alternate layers of an undoped polycarbonate and the same

polymer with  $\text{PbPc}(\text{CP})_4$ . The film has 4096 layers and an average layer thickness of 87 nm. The reflectivity of this multilayer at 590 nm as a function of time after an 800 femtosecond (FWHM) pump laser is incident on the layered sample is shown in Figure 2. The reflectivity increases with intensity. The response time was essentially within the laser pulse width.

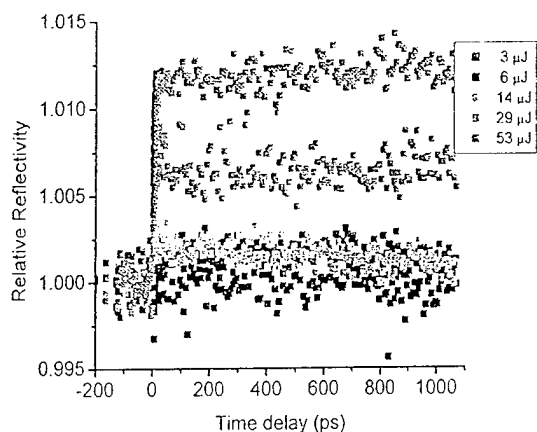


Figure 2. The Reflectivity of a sample with 4096 layers. Layers of pure polycarbonate alternated with layers containing the nonlinear dye  $\text{PbPc}$ .

In the case of samples dyes with nigrosine, where we presume the nonlinear response is predominately thermal change in the real part of the refractive index, a delay of a few hundred picoseconds before the reflectivity change was observed. We presume this is because the thermal response is slower than the electronic changes in the refractive index in the  $\text{PbPc}(\text{CP})_4$  dyed sample. The dynamics of the generation of the reflectivity in this case is being investigated theoretically.